PB81-192098

Comparison of Photochemical Behavior of Various Humic Substances in Water II. Photosensitized Oxygenations

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23 March 1981	ERL-Ath-290	☐ YES ☒ NO ☐ N/A	☒ YES ☐ NO ☐ N/A

5. PRESENT TITLE: Comparison of Photochemical Behavior of Various Humic Substances in Water: II. Photosensitized Oxygenations

a. TECHNICAL INFORMATION PLAN TITLE AND REFERENCE: Kinetics Studies of Photosensitized Oxygenations Induced by Humic and Fulvic Acids (FY80) ~~Research Comm. J PE AARB1A~~

6. AUTHOR, ORGANIZATION, AND ADDRESS:
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EPA PROJECT DOCUMENTATION

7. SERIES	8. REPORT DATE	9. CONTRACT/GRANT/IAG NUMBER
EPA-600/J-81-127	Journal Article	

10. TYPE OF MATERIAL (✓ one)
SPECIFY (WHERE NECESSARY)

- ☐ RESEARCH REPORT
- ☐ MEETING/PUBLICATION
- ☐ PROJECT REPORT AND PROJECT SUMMARY
- ☐ APPLICATIONS GUIDE
- ☒ JOURNAL PUBLICATION — Chemosphere. 10(1):119-126,1981.
- ☐ SUMMARY/SYNTHESIS
- ☐ UNPUBLISHED REPORT
- ☐ RESPONSE REPORT
- ☐ AUDIO VISUAL

11. PROJECT OFFICER/IN-HOUSE AUTHOR

a. SIGNATURE	b. DATE
Richard G. Zepp	3/23/81
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12. TECHNICAL INFORMATION (PROGRAM) MANAGER

a. SIGNATURE	b. DATE
Robert C. Ryans	24 March 1981
c. TYPED NAME AND ADDRESS	**d. FTS TELEPHONE NO.**
Robert C. Ryans Athens ERL	250-3306

13. COMMENTS

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TECHNICAL REPORT DATA
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1. REPORT NO.	2.	3.
EPA-600/J-81-127	Journal Article	PB81-192098

4. TITLE AND SUBTITLE	5. REPORT DATE
Comparison of Photochemical Behavior of Various Humic Substances in Water: II. Photosensitized Oxygenations	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Richard G. Zepp, George L. Baughman, and Patricia F. Schlotzhauer	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory U.S. Environmental Protection Agency College Station Road Athens, GA 30613	A28B1A 11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S. Environmental Protection Agency- Athens GA Environmental Research Laboratory College Station Road Athens, GA 30613	Journal Article 14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES Published in: Chemosphere. 10(1): 119-126, 1981.
Contact: R.G. Zepp, FTS 250-3428

16. ABSTRACT

The photochemical oxygenation of 2,5-dimethylfuran (DMF) in water was studied under a variety of reaction conditions employing various humic substances as photosensitizers. As predicted by theory, the reactions at low DMF concentrations were first order with respect to DMF, and the reaction rate constants were directly proportional to the average light intensity and to the concentration of humic substance. The rate of oxygenation photosensitized by the humic matter from a river was independent of hydrogen ion activity in the pH 5 to 9 range. Wavelength studies indicate that oxygenations photosensitized by humic substances are induced by ultraviolet and blue radiation. Rate constants computed for this photosensitized reaction in sunlight were in close agreement with experimental values. Calculations also show that the ratio of the sunlight rate constants to total visible solar irradiance (400 to 700 nm) is approximately constant. Therefore, it may be possible to calibrate rate constants for photosensitized reactions in terms of commonly measured units of visible light intensity such as foot candles.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

PRODUCT OF:
NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	8
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

Chemosphere Vol. 10, pp 119 - 126
Pergamon Press Ltd. 1981. Printed in Great Britain

0045-6535/81/010119-08$02.00/0

EPA-600/J-81-127
Journal ARticle

COMPARISON OF PHOTOCHEMICAL BEHAVIOR OF VARIOUS HUMIC SUBSTANCES IN WATER: II. PHOTOSENSITIZED OXYGENATIONS

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ABSTRACT -- The photochemical oxygenation of 2,5-dimethylfuran (DMF) in water was studied under a variety of reaction conditions employing various humic substances as photosensitizers. As predicted by theory, the reactions at low DMF concentrations were first order with respect to DMF, and the reaction rate constants were directly proportional to the average light intensity and to the concentration of humic substance. The rate of oxygenation photosensitized by the humic matter from a river was independent of hydrogen ion activity in the pH 5 to 9 range. Wavelength studies indicate that oxygenations photosensitized by humic substances are induced by ultraviolet and blue radiation. Rate constants computed for this photosensitized reaction in sunlight were in close agreement with experimental values. Calculations also show that the ratio of the sunlight rate constants to total visible solar irradiance (400 to 700 nm) is approximately constant. Therefore, it may be possible to calibrate rate constants for photosensitized reactions in terms of commonly measured units of visible light intensity such as foot candles.

INTRODUCTION

Mathematical models that forecast exposure concentrations of chemicals in aquatic environments require equations and quantitative data concerning rates of various environmental processes (1). In the area of photochemistry, the main emphasis has been on predicting direct photolysis rates of chemicals in water at low concentrations (2). Other photochemical processes, however, are also important for some chemicals. Studies in sunlight have shown that aquatic humus, the decayed plant material in lakes, rivers, and the sea, can photosensitize several different types of reactions of synthetic organic chemicals (3).

The general purpose of the research reported in this paper is to provide some groundwork for forecasting rates of photosensitized reactions in natural waters. Equations that describe photosensitized reactions are presented. The photosensitized oxidation of 2,5-dimethylfuran (DMF) (4) is employed as a tool to learn how variations in reaction conditions affect the photosensitizing efficiencies of various humic substances. Results of the studies are used (1) to compare the photosensitizing capacity of an aquatic humus and several soil-derived humic acids that were obtained commercially and (2) to compute rates of photosensitized oxidation in sunlight.

EXPERIMENTAL

Materials and Equipment. The sources of materials and the equipment used in this study are described elsewhere (3).

Procedures. Solutions of the humic acids were prepared as described elsewhere (3) as are procedures for studying DMF reactions in water (4). For the pH effect studies, the pH in Aucilla River water or rose bengal solution was adjusted by addition of an appropriate 0.01 M phosphate buffer hydrochloric acid or sodium hydroxide solution.

Spectral response functions for the photosensitized oxygenation of dimethylfuran were obtained using a photochemical merry-go-round apparatus (5). Monochromatic light was isolated from a 450-watt medium pressure lamp using the following filter combination and filter solutions: 313 nm, a Corning 7-54 glass filter, a 1-cm-thick solution of 0.001 M potassium chromate and 3% potassium carbonate, and 4 mm of pyrex glass; 366 nm, a Corning 7-54 and 0-51 filter combination; 405 nm, a combination of Corning 3-75, 4-70, and 7-51 filters; 436 nm, a Corning 3-73 and 5-58 glass filter combination; 546 nm, a glass filter combination consisting of Corning 3-68, 4-72, and 1-60 components. The response function was computed using eq. 1

$$X_{s,\lambda} = \frac{k_{s,\lambda}}{E_o^{av}(\lambda)} \tag{1}$$

where $k_{s,\lambda}$ was the rate constant (in sec^{-1}) for the photosensitized reaction at wavelength λ and $E_o^{av}(\lambda)$ was the average scalar irradiance in the reaction cell. Scalar irradiance is discussed below. The average irradiance was computed using eq. 2.

$$E_o^{av}(\lambda) = I_\lambda \frac{1 - 10^{-\alpha_\lambda \ell}}{2.303\ \alpha_\lambda} \tag{2}$$

where α_λ was the decadic absorption coefficient of the natural water sample in cm^{-1} at wavelength λ and ℓ was the cell pathlength in cm that was calibrated as described elsewhere (6). The light intensity term I_λ, which equals the number of photons that enter the system per unit volume and unit time, was measured using ferrioxalate actinometry (7). Reaction cells that were identical to the cells used in the natural water studies were filled with the same volume of 0.15 M ferrioxalate solution. The I_λ term was computed using eq. 3 where $\phi_{Fe^{2+}}$ is the quantum efficiency for ferrous ion production at λ (7) and F_λ, the fraction of light absorbed by the actinometer. (F_λ was essentially unity at all λ but 546 nm.) When the rate of Fe^{2+} production is expressed in units of moles/(liter sec), I_λ computed by eq. 3 is in units of einsteins/(liter sec) and $E_o^{av}(\lambda)$ is in units of millieinsteins cm^{-2} sec^{-1}, then

$$I_\lambda = \left(\frac{\text{Rate of } Fe^{2+} \text{ production}}{\phi_{Fe^{2+}} F_\lambda} \right)_\lambda \tag{3}$$

RESULTS AND DISCUSSION

Theory. In a well-mixed aqueous system containing a very low concentration of a chemical, both direct and photosensitized reactions can be described by first-order rate equations. The rate constant for photolysis, k_p, expressed in reciprocal time can be subdivided into components attributable to direct photolysis k_d and photosensitized reaction k_s (eq. 4).

$$-\frac{d[P]}{dt} = k_p[P] = (k_d + k_s)[P] \tag{4}$$

where $-d[P]/dt$ is the rate and $[P]$ is the concentration of the reactive chemical. At a given wavelength, the rate constant for each process is proportional to the average "scalar irradiance" E_o^{av}, expressed as number of photons per unit area and time. Scalar irradiance is the integral of a radiance distribution at a point over all directions about the point, and it is essentially a measure of the photon density at a point. Photochemists often loosely refer to scalar irradiance as the "light intensity." The concept of scalar irradiance is discussed more thoroughly elsewhere (8).

It was previously shown that the rate constant for direct photolysis k_d equals $k_a\phi_r$ where ϕ_r is the reaction quantum yield and k_a is the specific light absorption rate (2). In the remainder of this section, equations that generally describe photosensitized reactions are discussed.

The rate of any photochemical process is determined by the rate of light absorption I_a and the quantum yield for the process, ϕ (eq. 5).

$$\text{Rate} = I_a\phi \tag{5}$$

In photosensitized reactions, light is absorbed by the sensitizer molecules whose rate of light absorption $I^{s}_{a,\lambda}$ at wavelength λ is

$$I^{s}_{a,\lambda} = \frac{2.3}{j} \epsilon_{\lambda,s} E^{av}_{o}(\lambda) [S] \quad (6)$$

where $\epsilon_{\lambda,s}$ is the molar absorptivity of the sensitizer, [S] is the molar concentration of the sensitizer, and j is a constant that converts $E^{av}_{\delta}(\lambda)$ into units compatible with the other terms in eq. 6. When $E^{av}_{\delta}(\lambda)$ is expressed in units of photons cm^{-2} sec^{-1}, j equals 6.02×10^{20}; j equals one when $E^{av}_{\delta}(\lambda)$ is expressed as millieinsteins cm^{-2} sec^{-1} as in the experiments with monochromatic light described in this paper.

The expression for the quantum yield of a photosensitized reaction varies from one type of reaction to another and can, in some cases, be quite complex. With a very low concentration of the reactive chemical present in the system as is usually the case in the environment, the presence of the chemical has a negligible effect on the lifetime of the electronically excited sensitizer or other short-lived species derived thereform. Under these conditions the reaction quantum efficiency is proportional to [P], i.e., $\phi = Q_{\lambda}[P]$ where Q_{λ} is some constant. The complete rate expression for a photosensitized reaction is thus:

$$-\left(\frac{d[P]}{dt}\right)_{\lambda} = \frac{2.3}{j} E^{av}_{o}(\lambda) \epsilon_{\lambda,s} Q_{\lambda} [S][P] = k_{s,\lambda}[P] \quad (7)$$

With constant sensitizer concentration, as is usually the case, the rate expression is in first order form.

Light attentuation effects must be considered in evaluating kinetic data for photosensitized reactions. When the absorbance in a system $a_{\lambda}\ell$ is less than 0.05, then the fraction of light absorbed, $1-10^{-a_{\lambda}\ell}$, approximately equals $2.3\ a_{\lambda}\ell$. Under these conditions $E^{av}_{\delta}(\lambda)$ equals $I_{\lambda}\ell$ (see eq. 2), and the rate constant for photosensitized reaction is predicted to be approximately proportional to the sensitizer concentration, [S] (see eq. 7). At the other extreme, with absorbances in excess of 2, essentially all of the light is absorbed and $1-10^{-a_{\lambda}\ell}$ is about 1. Under these conditions $E^{av}_{\delta}(\lambda)$ is inversely proportional to the decadic absorption coefficient a_{λ} (see eq. 2). If the sensitizer is the only light absorber in the system, i.e., if $a_{\lambda} = \epsilon_{\lambda}[S]$, then it follows from eq. 7 and the above that, when $a_{\lambda}\ell$ exceeds two, the rate constant is predicted to become independent of sensitizer concentration ($k_{s,\lambda} = Q_{\lambda}/j\ell$). The same is true if the sensitizer absorbs a constant fraction of the light absorbed by a mixture. At concentrations of humic substances that do not exceed what is found in natural waters, absorbances with a 1-cm pathlength cell are sufficiently low that the rate constants should depend on the concentration of humic substances.

Humic substances are probably mixtures of several components, only some of which may actually photosensitize reactions. To compare photosensitizing capacities of such mixtures, it is necessary to correct for various system specific effects on rate constants. In this paper, response functions $X_{s,\lambda}$ computed by eq. 1 are used for this purpose. The response function, like the reaction quantum yield, is independent of system-specific factors such as light attenuation and intensity. As shown by eq. 8, $X_{s,\lambda}$ theoretically depends on the strength of light absorption by the sensitizer(s) in the system, as reflected by $\epsilon_{\lambda,s}$, the sensitizer concentration [S], and the quantum efficiency, which is proportional to Q_{λ}.

$$X_{s,\lambda} = 2.3\ \epsilon_{\lambda,s} Q_{\lambda} [S] \quad (8)$$

If a single substance within the mixture of substances that comprise humic substances were the photosensitizer, a plot of $X_{s,\lambda}$ versus wavelength, that is, the "action spectrum," would parallel its absorption spectrum.

Introduction to experimental studies. The light-induced reaction of 2,5-dimethylfuran in aqueous solutions of various humic substances was studied to determine the effects of variations in reaction conditions. This reaction was selected for several reasons. First, DMF was previously shown to be unreactive in distilled water (3,4). Thus, the reaction in solutions of humic substances was entirely photosensitized. Second, the DMF reaction was conveniently rapid in sunlight and in monochromatic light isolated from a mercury arc lamp. Third, DMF was unreactive in the dark, at least over the periods of time consumed by most of the photochemical experiments described below. Finally, results obtained by Zepp and co-workers (4) and more recently by Mill and co-workers (9) indicate that the predominant mechanism for photosensitized

oxidation of DMF involves a rapid intermediate step in which sensitizers in their triplet states transfer energy to molecular oxygen to form singlet oxygen. Other mechanisms involving light-induced generation of hydroxyl or alkylperoxy radicals are unlikely to play a significant role in the photooxidation of DMF, because the steady-state concentrations of these radicals have been shown to be very low in sunlight-exposed natural waters containing high concentrations of humic substances, including the same Aucilla River water used in these studies (9). Because other photosensitized reactions involve triplet sensitizers, results of this detailed study may have general applicability. This point is discussed in more detail elsewhere (10).

Variation in sensitizer concentration. Typical results of the effects of varying the concentration of humic substances on the rate constant k_S and the response function X_S for photosensitized reaction of dimethylfuran determined with monochromatic light (366 nm) are shown in Table 1. As predicted by eq. 8 the response function is directly proportional to the concentration of the aquatic humus. The rate constant was not directly proportional to concentration because at higher concentrations of humic acid, light attenuation effects partially offset the enhancement in k_S caused by the increase in the response function.

Table 1. Kinetic parameters (366 nm) for photosensitized oxygenation of 2,3-dimethylfuran in Aucilla River water mixed with distilled water to yield solutions containing various concentrations of aquatic humus.

Concentration, mg org C/liter	k_S, hr^{-1}	X_S, 366
21	0.18 ± 0.02	23 ± 3
15	0.13 ± 0.01	15 ± 1
10	0.077 ± 0.007	8.6 ± 0.6
6.3	0.056 ± 0.005	6.0 ± 0.6
2.1	0.026 ± 0.002	2.7 ± 0.3

pH Variation. The effects of pH change were investigated by altering the pH of the Aucilla River water through addition of phosphate buffer, sulfuric acid, or sodium hydroxide. Increasing the pH caused increases in the light absorbance of the substances in the river water. We anticipated that these changes in light absorption, which indicated speciation changes, would be accompanied by changes in rate constants for the dimethylfuran photooxidation. However, rate constants for the reaction in sunlight were actually constant in the pH 5 to 9 range (Figure 1). At pH values lower than this range, the reaction rate constant increased somewhat and at pH values greater than 10, the rate constant decreased. Comparisons with unbuffered river water indicated that the phosphate buffer has no effect on the rate constant (Figure 1).

The pH effects observed in the Aucilla River water could be caused by changes in speciation of the natural photosensitizers in the water or, alternatively, could be attributable to changes in the quantum efficiency for the reaction itself. To clarify this point, the DMF reaction was studied in water buffered as above, but employing rose bengal as the photosensitizer. The absorption spectrum of rose bengal, a known sensitizer of singlet oxygen reactions, did not change when the pH was raised from 5.5 to 11, indicating no speciation changes. However, pH changes affected the rate constant for the rose-bengal-sensitized oxidation of DMF, in the same way as in the Aucilla River water (Figure 1). At pH values greater than 10, the rate constant decreased.

One possible interpretation of these data is that the components(s) of the humic substances that photosensitize the formation of singlet oxygen do not ionize in the pH 5 to 9 range. If so, this precludes the possibility that the photosensitizing component(s) are species such as phenols or carboxylic acids that are known to ionize in this pH range. That the decrease in rate constant at pH 10 is about the same with both rose bengal and humic substances as photosensitizers indicates that the same factor is responsible for the decrease with both photosensitizers. This decrease may be attributable to quenching of singlet oxygen by hydroxide ion.

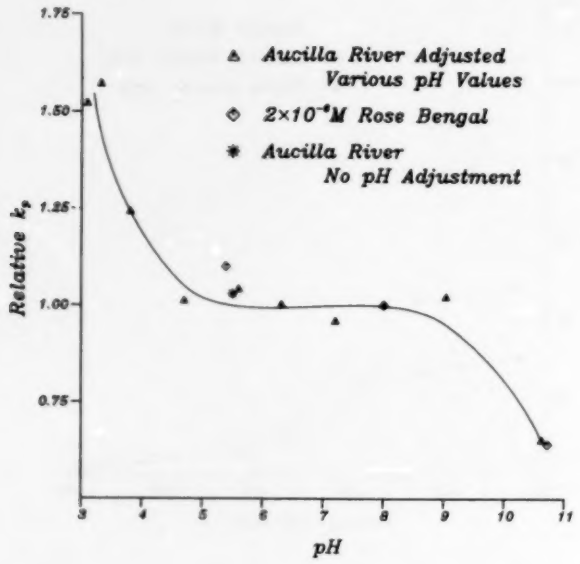

Figure 1. pH Dependence of Photosensitized Oxygenation of 2,5-Dimethylfuran

Wavelength studies. A series of kinetic studies was conducted to determine the response functions of photosensitized oxygenation as a function of wavelength, i.e., the "action spectra" for the photosensitized reactions. These action spectra provide a means of quantitatively comparing the photosensitizing abilities of aquatic humus and two commercial humic acids. Also, action spectra can be used for computation of photolysis rate constants in sunlight as discussed in the following section. As shown in Figure 2, action spectra for the reaction of dimethylfuran sensitized by aquatic humus or the humic acids were the same within a factor of 2 at wavelengths in the near ultraviolet and visible region (366, 405, 436, and 540 nm). In the UV-B region (313 nm), however, the aquatic humus was found to be much more effective than the commercial humic acids.

Computation of rate constants in sunlight. Near surface rate constants for photosensitized oxygenation of DMF in sunlight (Figure 3) were computed as a function of wavelength using computer-generated sunlight intensities (2), the response functions shown in Figure 2, and eq. 1. Figure 3 indicates that ultraviolet light is most effective at promoting the reaction sensitized by the aquatic humus and blue light is most effective with the humic acids. Although the response function for aquatic humus is much larger than for the humic acids in the 300 to 330 nm spectral region, the influence of this difference on the sunlight rate constants is much diminished by the considerably lower intensity of sunlight in this spectral region. By using the computer to integrate the computed values of $k_{s,\lambda}$ over all wavelengths, sunlight rate constants were obtained which indicated that the half-lives should be 5 to 10 minutes at midday during summer and that relative rate constants should be: Aldrich humic acid, 1.2; Aucilla River, 1.0; and Fluka humic acid, 0.80. These computed values agree closely with those actually observed (3,4).

The computer was also used to compute the ratio of near-surface rate constants for the DMF reaction to the integrated intensity of visible sunlight that is incident on the water surface. These ratios were approximately constant at all but the lowest solar altitudes (Table 2), indicating that it may be possible to calibrate rate constants for photosensitized reactions in terms of some widely measured units of sunlight intensity such as foot candles.

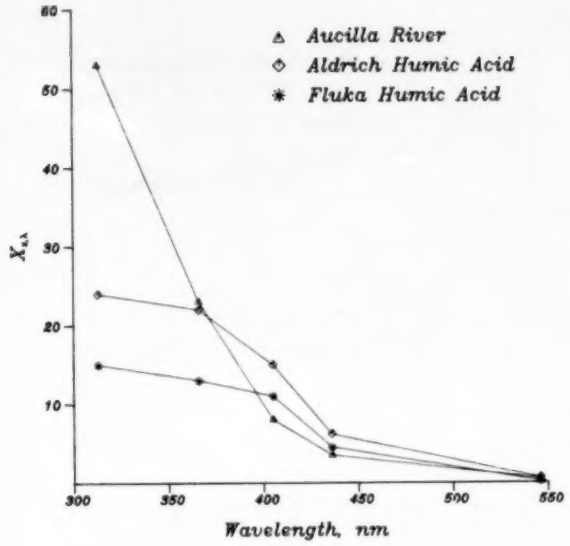

Figure 2. Action Spectra for Photosensitized Oxygenation of 2,5-Dimethylfuran. Reaction conditions: absorbance of each solution at 366 nm was adjusted to 0.20 in a 1.00 cm cell; pH was adjusted to 6.0.

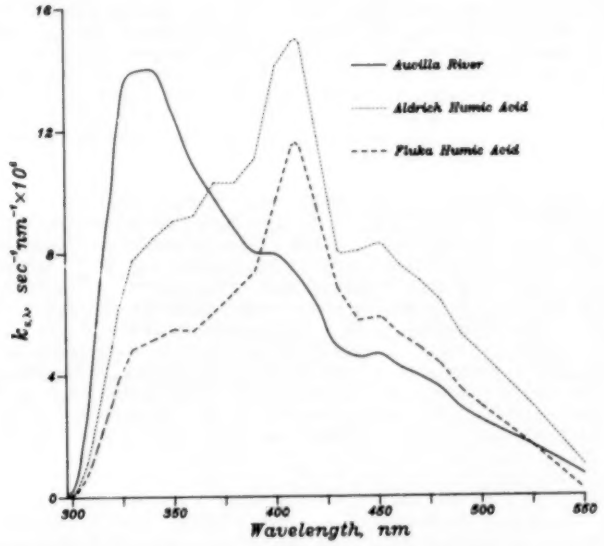

Figure 3. Wavelength Dependence of Rate Constants Computed for Photosensitized Reaction of 2,5-Dimethylfuran in Sunlight (Midday, Summer, Latitude 40°N). Rate constants, k_s, integrated over the entire spectral region are: Aucilla River, 0.54 hr^{-1}; Aldrich humic acid, 0.65 hr^{-1}; Fluka humic acid, 0.43 hr^{-1}.

Table 2. Computed ratios of rate constants k_s (sec^{-1}) for photosensitized oxygenation of 2,5-dimethylfuran to total visible solar irradiance on a horizontal plane E ($W\ cm^{-2}$).

Solar Altitude	$\frac{k_s}{E} \times 10^2$, $cm^2\ W^{-1}\ s^{-1}$ [a,b,c]		
	Aucilla River	Aldrich humic acid	Fluka humic acid
90	3.92 (1)	4.46 (1)	2.73 (1)
80	4.23 (1.08)	4.81 (1.08)	2.94 (1.08)
70	4.30 (1.10)	4.89 (1.10)	3.00 (1.10)
60	4.39 (1.12)	5.02 (1.12)	3.07 (1.12)
50	4.45 (1.14)	5.16 (1.16)	3.16 (1.16)
40	4.51 (1.15)	5.31 (1.19)	3.25 (1.19)
30	4.52 (1.15)	5.41 (1.21)	3.32 (1.22)
20	4.67 (1.19)	5.66 (1.27)	3.47 (1.27)
10	5.57 (1.42)	6.76 (1.51)	4.14 (1.52)

[a]Computed using data in Figure 2, irradiance values from Cline and Zepp's Solar program (2) and eq. 1. [b]For solutions with absorbance of 0.20 at 366 nm. [c]Relative values in parentheses.

CONCLUSIONS

Results of these studies indicate the following.

(1) At very low concentrations of pollutants, photosensitized reactions are first order with respect to pollutant. The first-order rate constants are directly proportional to sensitizer concentration in systems that weakly absorb light. Reactions become independent of the concentration of photosensitizer, however, when all the active light is absorbed.

(2) The rate constants for an oxidation photosensitized by aquatic humus were found to be independent of hydrogen ion activity from pH 5 to pH 10. Above pH 10, the rate constants decrease with increasing pH.

(3) Oxidations that are photosensitized by humic substances are mainly induced by ultraviolet and blue radiation.

(4) Employing action spectra determined in this study and computer-generated sunlight intensities, rate constants for photosensitized reactions were calculated and found to be in close agreement with experimental values determined in sunlight. The computations indicate that it should be possible to calibrate the rate constants in terms of commonly measured units of intensity such as foot candles.

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(Received in USA 9 December 1980)